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1. Your reference — NS/99096GB

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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

IMPERIAL COLLEGE OF SCIENCE,
TECHNOLOGY & MEDICINE
Exhibition Road,
London SW7 2AZ,
England

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation — 60507 6600S.

4. Title of the invention — "Island Arrays"

5. Name of your agent *(if you have one)* — BATCHELLOR, KIRK & CO.

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

102 - 108 Clerkenwell Road,
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Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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11. I/We request the grant of a patent on the basis of this application.

Signature	Date
Batchellor Kirk & Co	17th August 1999

12. Name and daytime telephone number of person to contact in the United Kingdom

Batchellor, Kirk & Co.
Mr. N. Shindler - 0171-253-1563

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"Island Arrays"

This invention relates mainly to semi-conductor device fabrication, and in particular to methods of fabricating semi-conductor devices in materials such as silicon or gallium arsenide, or other III-V compounds.

Where it is required to produce arrays of large numbers of semi-conductor devices in a single "wafer" of material, it is of course possible to produce a regular pattern, by means of methods such as electron-beam lithography or photolithography and successive masking stages. However, such methods do require quite complex equipment and preparations, particularly when it is required to make large arrays of very small devices, because this requires the preparation of correspondingly detailed art work and the required optical resolution is difficult to attain.

Consequently there is a need to be able to make (ca. 1 to 0.01 micron) feature size structures on semiconductor wafers and other thin solid substrates by a fast and practical method. With such a method it would for example be possible to make dense arrays of field emitting structures and other devices needing high densities of special features. The method of controllable island lithography is a solution to this problem.

The process of island lithography has several major process steps. The first major stage is the deposition of a thin film of a highly soluble solid onto the material on which the features are to be made; followed by exposure to a fixed vapour pressure of the solvent in which the deposited layer is soluble. Such treatment causes the deposited thin film to re-organise from being a thin film into an array of hemispherical islands. The second major processing stage is to employ these islands as resist in a reactive etching process so as to obtain arrays of pillar like structures or arrays of cones. The essential point about reactive etching is that it is directional, etching downwards on to the surface much faster than side wise. This is in contrast to simple liquid phase etching that is homogeneous in behaviour, etching equally in all directions at the point of contact.

One such system which has previously been proposed, depends on the effect that very thin films of cesium chloride deposited on a hydrophilic substrate when exposed to water vapour under controlled conditions will re-organise into a hemispherical island array. The characteristics of the array are that it is disordered and near to Gaussian in

size distribution: the array is described by a fractional coverage (F) called "packing density", with islands of a mean diameter (<d>), having a particular standard deviation. This technique can be used as a well controlled process for producing island arrays of known characteristics on silicon surfaces, with mean diameters ranging from 30 to 1200nm (ca.±17%). Distributions of such CsCl island arrays have previously been used[2] as a resist in the RIE (reactive ion etching, chlorine based) fabrication of mesoscopic pillar structures on n^+GaAs. The measured photo luminescent spectra showed large band gap increases arising from quantum confinement effects. There have been other proposed approaches to nano-scale lithography using condensation effects leading to self-organizing systems[3-5], e.g. metal nuclei have been used to fabricate dense arrays of field emission tips[6,7].

The present invention relates to an important extension to this process that makes it more useful and versatile and involves the addition of a major process step between the deposition and etching processes which turns the overall process from a positive to a negative process.

Thus, the present invention can provide a method of device fabrication in silicon, silicon dioxide, gallium arsenide, indium antimonide and other etchable solids for the production of cones and wells.

Accordingly the present invention provides a method of semi-conductor device fabrication in which "negative" regions for defining individual devices of an array are formed by the steps of:

a) depositing a very thin film of a highly soluble solid onto a flat hydrophilic substrate;

b) exposing the film to solvent vapour under controlled conditions so that the film reorganises into an array of discrete hemispherical islands on the surface;

c) evaporating a film of a suitable resist material over the whole surface;

d) removing the hemispherical structures together with their coating of resist leaving a resist layer with an array of holes corresponding to the islands; and

e) subjecting the resulting structure to a suitable etching process so as to form a well at the position of each hole.

The highly soluble solid may be a salt such as cesium chloride, in which case the solvent used will be water. The substrate may for example be an SiO_2 layer on Si, or gallium arsenide or indium antimonide. Preferably the resist material is aluminium, and

in a preferred embodiment of the invention, the removal of the coated hemispherical structures is achieved by submerging the structure in an ultrasonic agitation bath filled with solvent that has the effect of dissolving the islands and thus removing the thin layer of material in which they were coated, leaving a perforated film over the rest of the substrate, namely covering the "ocean" area in which the islands are located. This process step is known as a "lift-off" process. This perforated film whose holes correspond to the now removed islands can act as a resist in an etching process.

The etching may be by reactive ion etching whereupon the holes in the resist are etched to make well like structures. In this negative resist case it is also possible to use laser assisted etching to make well like structures because laser etching is directional, etching faster in the direction of the laser beam than sidewise to the beam.

A variant to the "lift-off" process described above is to add directionality, so creating an anisotropic system. If instead of depositing a resist film over the islands and substrate by direct downwards evaporation the vapour stream is directed at an angle that is a grazing angle to the substrate, the islands will cast a deep shadow in which there will be no deposition of material. In this way the holes in the film remaining after "lift-off" will be oblong, nearly elliptical, in shape and all with their long axis in the same direction. The wells made by etching will follow the shape of these elliptical holes in the thin film resist. It is a step in the fabrication of certain anisotropic composite materials.

The first application of this island resist method as a positive resist scheme was in the fabrication of arrays of pillars in gallium arsenide. In this case a thin layer of cesium chloride was thermally evaporated onto a wafer of gallium arsenide whose surface had been treated so that it was hydrophilic. The coated wafer was placed in a chamber at a controlled vapour pressure of water for a fixed period of time. This treatment causes a multi-layer of water to condense on the surface of the cesium chloride and also the substrate when it becomes unmasked. The island array develops and grows as a result of the presence of this liquid layer in which the cesium chloride is soluble. The resulting island array has a certain average island diameter and a population of islands with a Gaussian distribution and a particular width at half full height and a particular packing density.

Some embodiments of the invention will now be described by way of example with reference to the accompanying illustrations in which:

Figure 1a illustrates the deposited layer of CsCl on the SiO_2/Si;

Figure 1b illustrates the formation of CsC1 islands on the substrate;

Figure 1c shows the formation of an Al film over the structure of Figure 1b;

Figure 1d shows the structure of Figure 1c after ultrasonic agitation;

Figure 1e shows the effect of subjecting the structure of Figure 1d to RIE;

Figure 2 is a perspective view of a "tip-array" formed using CsC1 as resist;

Figure 3 is a graph of wall-angle and etch-rate ;

Figure 4 is a perspective view of pillars formed by CsC1 hemispheres acting as resist;

Figure 5 is a plan view of an array of CsC1 hemispheres coated with Al;

Figure 6 shows the array of Figure 5 after removal of the hemispheres;

Figure 7a is a perspective view of wells formed in SiO_2 on Si; and

Figure 7b is a perspective view of a sectioned well in the structure of Figure 7a.

Methods of CsCl island fabrication are explained in detail in references (1) and (2). Briefly the silicon substrate coated in native oxide (both n- and p-type samples can be used) are etched and washed so as to give a reproducible hydrophilic surface. CsCl is evaporated on the surface. The CsCl coated substrate is then transferred (under dry conditions) to a chamber of fixed water vapour pressure. The thin film of CsCl develops into an island array of hemispheres whose dimensional characteristics depend upon initial thickness, water vapour pressure and time of development. The developed substrate is transferred to the scanning electron microscope under unchanged humidity, where the island array can be photographed for measurement.

Tip Fabrication

The tip fabrication illustrated in Figure 2 resulted from using the humidity value of the prevailing laboratory conditions (40%) and the CsCl thickness and development time were then chosen to give the desired distribution. The development time was the time elapsed from removing the CsCl coated silicon from the deposition chamber to the RIE chamber at the moment of its pump down. The fabrication of tips was carried out on n-type and p-type silicon substrates of {100} orientation as described above. Etching was carried out in equipment obtained from Oxford Plasma Technology (model RIE80, fitted with a 6.5" table). The conditions for island growth were:- CsCl thickness 66Å; relative humidity 40%; and 5 min. exposure time. This resulted in an array of hemispherical islands with packing density 0.18, and mean diameter 850Å ± 200 Å. This CsCl/Si

system, placed upon a silica glass plate in the RIE apparatus, was etched for 3 minutes in a gaseous mixture made by combining O_2: Ar: CHF_3 in a ratio of flow rates of 1: 10: 20 sccm. The total chamber pressure was 40 millitorr, the total rf power was 155 watts and the dc bias was 400 volts. This process resulted in the tip array shown on Fig 2. For these conditions we measured a tip angle of ca. 28°. The tip diameter is not observable in our sem. and must be <100Å.

It is possible to form regular cones with a required wall angle (the angle that the side makes with the horizontal) by controlling the etching process. Figure 3 shows the wall angle as a function of total pressure for a 1:10:20 mixture; average power 61 watts; 300 dc bias. The relation of wall angle to some of the other independent variables is not shown, but the trends are as follows. There is an increasing etch rate with increasing dc bias; comparative insensitivity to Ar flow rate, at least for plus/minus a factor of two in flow-rate; and, wall angle and etch rate both increase with increasing CHF_3 flow rate. When the total pressure is in excess of 75 millitorr we observe rough surfaces and the on-set of a component of horizontal silicon etching, as evidenced by under-cutting of the CsCl: this is shown in Figure 4, for which the etching conditions were: 1:10:20 mixture; total pressure 87 millitorr; 73 watts; 300 volt dc bias; 15 mins. etching time. In general it can be seen that there is a shallow depression in the substrate around each pillar or tip. This shallow "trenching" can be ascribed to enhanced, proximity, sputtering arising from ions scattered from the vertical features[8].

Well Fabrication

The procedure for well fabrication, cf. Figure 1, is first to grow the CsCl island array on SiO_2 on Si: here we are interested in larger hemispheres, in the 0.5 to 1 micron range. A film of Al is then evaporated over this structure. and the Al film that coated the CsCl hemispheres is then caused to lift off. by means of ultrasonic agitation in water. The remaining Al can then act as a resist. enabling holes to be etched in the SiO_2.

In order to grow large hemispheres of CsCl comparatively thick films of CsCl are needed and it is necessary to expose these films to a relatively high humidity. As an example: using 1350Å thick CsCl, developed at 55% relative humidity for 92 hrs., gave an average hemisphere diameter of 9200±1460Å and a packing density of 35.4%. Figure 5 shows the CsCl islands coated by a 1050Å thick Al film. This array was made on a thermally grown oxide on silicon: the hydrophilic oxide was 3200Å thick. On to this CsCl/SiO_2 surface was evaporated pure Al to a thickness of 1060Å. The Al coated

structure was ultrasonically agitated for 2 minutes. The result was the complete removal, i.e. lift-off, of the Al which covered the CsCl, leaving an Al coating with an array of holes matching the developed CsCl array, as shown on Figure 6. This structure was subjected to RIE using Oxford Plasma Technology equipment (model RIE80, fitted with a 6.5" table). The $Al/SiO_2/Si$ system was placed upon a silica glass plate in the RIE apparatus under the following conditions:- feed-gas 10:20 sccm ($Ar:CHF_3$); total pressure 5 millitorr; at 160 watts and 220 dc. bias for 5 mins.: the resulting well structure is shown in Figures 7a and b.

Discussion

Cesium chloride is eroded by physical sputtering processes only, while the silicon is finally chemically removed. The selectivity, which is the rate of silicon etching to that of the cesium chloride, can be determined from the physical characteristics of the tip structures. Several possible cases can be considered. For the case that the sputtering rate, ω, of CsCl is uniform over the surface of the hemisphere, the time, T, for removal of a hemisphere of initial radius R_o is,

$$T = R_o/ \omega$$

While the resist is being sputtered away the silicon is being etched vertically, at a rate v, so that a conical structure results in the Si. The height, H, of the right regular cone will be.

$$H = R_o v/ \omega$$

The cone ("tip") angle ϕ is

$$\phi = 2 \tan^{-1} (\omega/v) = 2 \tan^{-1} (R_o/H)$$

For example, we have measured an average $\phi = 28^o$, this gives a value of $\omega/v = 4$, which is the selectivity. For the case where sputtering of CsCl is only by vertical removal, at rate α, the rate term ω is replaced by α in the above equations.

For vertical and horizontal CsCl sputtering (the latter being uniform in the plane parallel to the substrate) the relations are,

$$T = R_o/(\alpha^2 + \eta^2)^{1/2}$$

where η is the horizontal rate: and the tip angle is,

$$\phi = 2\tan^{-1}\left(\frac{(\alpha^2 + \eta^2)^{1/2}}{v}\right)$$

Thus the present invention enables the fabrication of pillars and cones of silicon in high packing density and of dimensions in the tens of nm region. Furthermore wells in silicone dioxide on silicon can be made by a lift-off process, again in high packing density. The relation of wall angle to process parameters in the RIE technique have been investigated and shown to be capable of control over a useful range of angles.

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9. H. Dimigen and H. Luthe, Philips Tech.Rev., Rev., 35 199 (1975).

Figure Captions

Figure 1. Lift-off scheme: A.SiO_2 on Si; B. CsCl islands developed on SiO_2; C. Al film evaporated on surface; D. Lift-off (ultrasonic agitation); E. Well fabrication using RIE.

Figure 2. Tip array fabricated by RIE using CsCl as a resist

Figure 3. Wall angle and etch rate as a function of total feed-gas pressure for constant chemical composition and electrical conditions.

Figure 4. Pillars with CsCl caps still in place. Bar length is 10 microns; view at 70° to normal

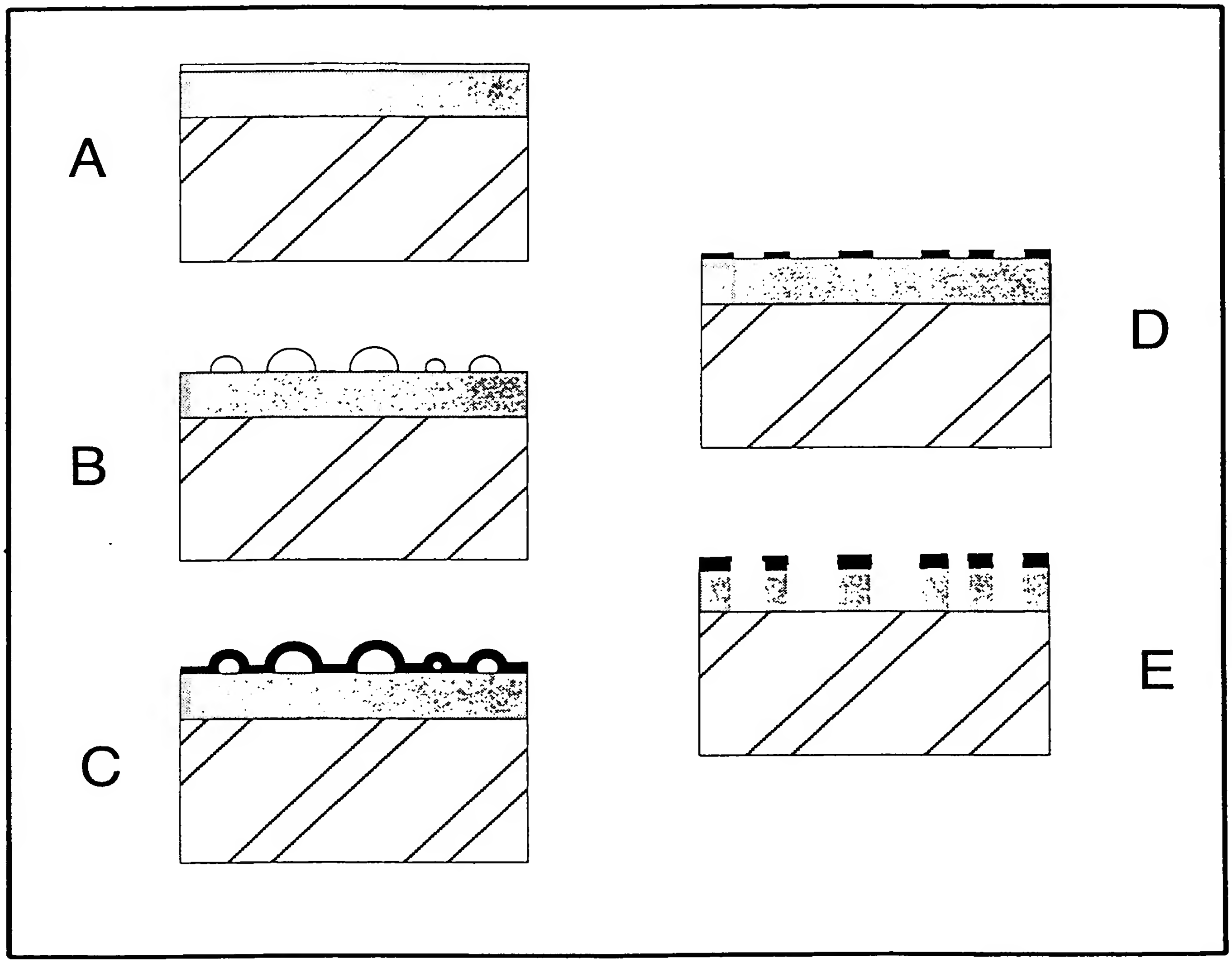
Figure 5. CsCl hemispheres on SiO_2, the whole coated in Al. (mag. 7.5K; 10 micron bar)

Figure 6. CsCl removed exposing SiO_2 and leaving the rest of the Al film intact.(mag.10K; 1 micron bars)

Figure 7a Wells in SiO_2 on Si. The Al layer coats the oxide. (viewed at 45°. mag 20K; 1 micron bars)

Figure 7b. Well in SiO_2, the Al layer is clearly visible (mag. 50K; 1 micron bars)

T,G,S,Fig 1



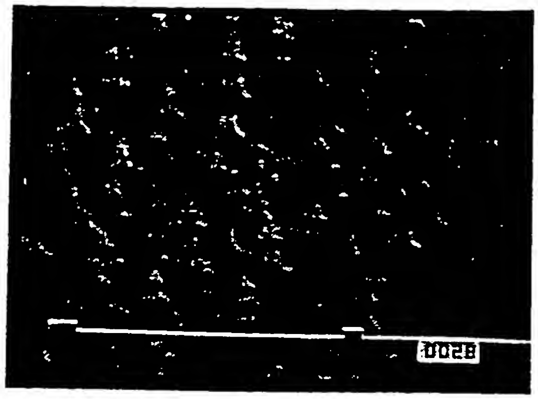


Figure 2. Tip array fabricated by RIE using CsCl as a resist

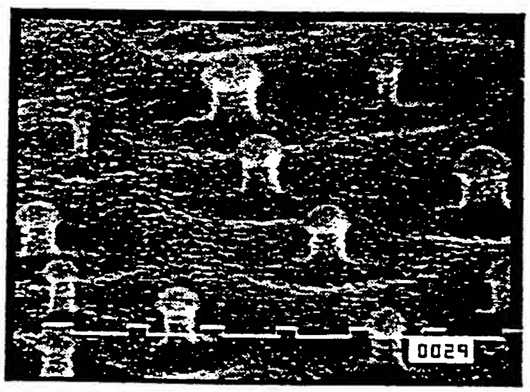
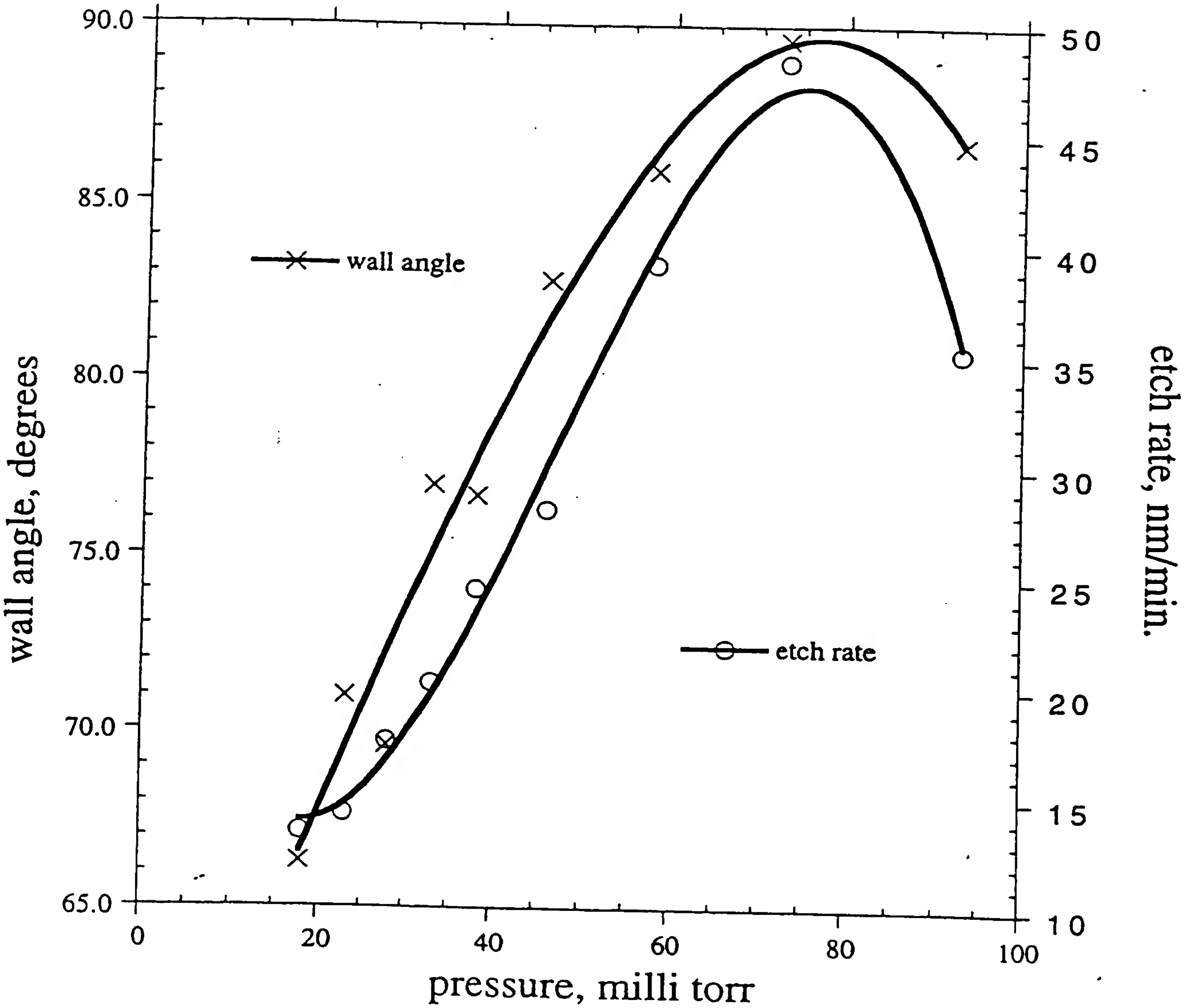


Figure 4. Pillars with CsCl caps still in place. Bar length is 10 microns; view at 70° to normal.



90.0
85.0
80.0
75.0
70.0
65.0
wall angle, degrees
wall angle
etch rate
0
20
40
60
80
100
pressure, milli torr
50
45
40
35
30
25
20
15
10
etch rate, nm/min.

FIG-5

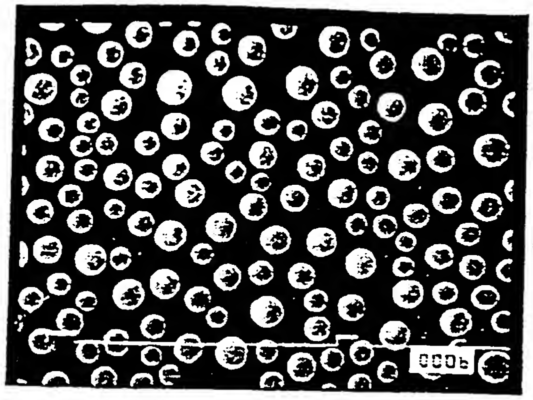


Figure 5. CsCl hemispheres on SiO_2, the whole coated in Al.
(mag. 7.5K; 10 micron bar)

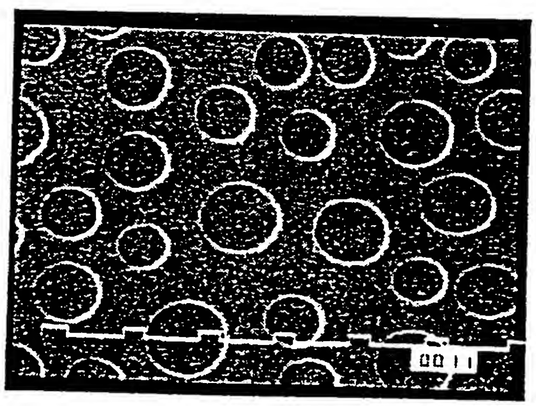


Figure 6. CsCl removed exposing SiO_2 and leaving the rest of the Al film. (mag.20K; 1 micron bars)

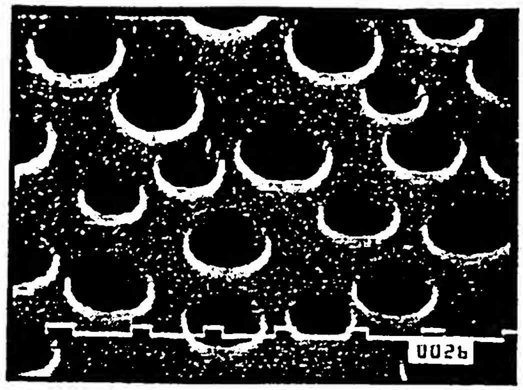


Figure 7a Wells in SiO_2 on Si. The Al layer coats the oxide.
(viewed at 45°. mag 20K; 1 micron bars)

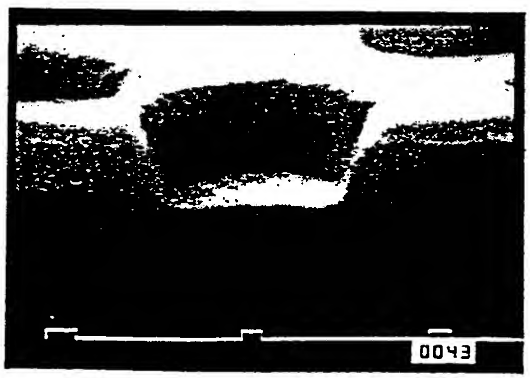


Figure 7b. Well in SiO_2, the Al layer is clearly visible (mag. 50K; 1 micron bars)